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Enhanced magnetic properties of NiO powders by the mechanical activation of aluminothermic reduction of NiO prepared by a ball milling process

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ABSTRACT

We report the effect of mechanical activation on NiO–Al (x wt%) reduction reaction and resulting structural and magnetic properties by carrying out high-energy planetary ball milling. The pure NiO (unmilled) and milled NiO–Al ($x \leq 2.5$) powders exhibit face centered cubic structure, but the antiferromagnetic nature of pure NiO powder shows significant room temperature ferromagnetism with moderate moment and coercivity after milling due to non-stoichiometry in NiO caused by the defects, size reduction and oxidation of Ni. On the other hand, the addition of Al between 2.5 and 10% in NiO forms solid solution of NiO–Al with considerable reduction in the moment due to the atomic disorder. With increasing Al above 10%, NiO reduction reaction progresses gradually and as a result, the average magnetization increases from 0.57 to 4.3 emu/g with increasing Al up to 25%. A maximum of 91% reduction was observed for NiO–Al (40%) powders in 30 h of milling with a large increase in magnetization ($\sim$24 emu/g) along with the development of α-Al_2O_3. Thermomagnetization data reveal the presence of mixed magnetic phases in milled NiO powders and the component of induced ferromagnetic phase fades out with increasing Al due to the formation of Ni from the NiO–Al reduction reaction. The changes in the structural and magnetic properties are discussed on the basis of mechanical activation on the reduction of NiO by Al. The controlled reduction reaction with different Al content in NiO–Al is encouraging for the applications in catalysis and process of ore reduction.

1. Introduction

Recently, the study of transition metal based oxides at nanoscale has received growing interest because of their novel properties [1] and potential applications in wide variety of technological areas such as sensor [2], supercapacitor [3], solar cell [4], battery [5], spintronics [6] and resistive random access memory [7,8]. In particular, the possibility of tuning the properties of nanostructured NiO has opened up novel pathways for extensive research activity in the nanoscale science. As a result, different scientific groups have employed various synthesis methods such as sol–gel [9], chemical precipitation [10], pyrolysis [11], hydrothermal [12], solid state [13], and ball milling [14], for the preparation of NiO nanostructures with various shapes and sizes. Among these techniques, high-energy planetary ball milling has been proven as a simple and inexpensive method for the synthesis of nanostructured alloy powders on large scale with controlled magnetic properties. This solid state method produces materials in the powder form with nanosized crystallites, which can be tailored in different shapes and dimensions by compacting and giving appropriate heat treatment for commercial exploitation. In addition, this technique is known to activate solid–solid and solid–liquid chemical reactions by utilizing mechanical energy supplied during milling and hence called as mechanochemical synthesis/reactive milling. Accordingly, several mechanochemical reactions have been reported for making *in-situ* nanocomposites and compounds [15,16] with improved mechanical properties such as strength and toughness [17]. It has been largely reported that there are two types of reaction kinetics depending on the milling conditions: (1) self-propagating combustion reaction needing a critical time for the ignition of the combustion reaction, when the reaction enthalpy is very high and (2) gradual or progressive reaction since the reaction extends through a small volume during each collision.

The solid state reaction of NiO–Al to produce Ni/Al_2O_3 nanocomposites was first reported by Matteazzi et al. [15] using dry milling under argon (Ar) atmosphere. Later, Oleszak [18] and Udhayabanu et al. [19] utilized the mechanical activation of

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aluminothermic reduction of NiO for the development of NiAl/Al_2O_3 and Ni/Al_2O_3 nanocomposites under different process controlling agent, respectively. These studies revealed that the effect of mechanical activation on the reduction of NiO by Al is reported to be gradual one [19]. Recently, Jeangros et al. [20] reported that the reduction of NiO by hydrogen in an environmental transmission electron microscope (TEM) results in Ni nucleation on NiO either by epitaxial or by the formation of randomly oriented grains. A careful review of the literature summarizes that the process of reduction in NiO is carried out randomly on limited compositions without any systematic investigations and detailed analyses of the resulting magnetic properties due to the reduction reaction are still missing. It may be noted that the study of NiO reduction and the control of properties of subsequent Ni are of practical importance in the fields of ore reduction [21], catalysis [22] and solid oxide fuel cells, for which it determines the structure of the electronic conductor on the anode side during operation [23] and resistive random access memory [7]. In addition, the NiO system exhibits novel properties when the size is reduced down to nanoscale [11,24,25]. Therefore, in the present study, we report a systematic investigation on the NiO–Al (*x* wt%) reduction reaction by means of dry ball milling in Ar atmosphere and the evolution of magnetic properties as a function of Al addition.

2. Experimental details

Weighed quantities of high purity (> 99.9%) NiO and Al powders corresponding to the mixture of NiO–Al (*x* wt%) with *x* varying from 0 to 40 were subjected to ball milling under high purity Ar atmosphere in a high-energy planetary ball mill. The milling process of NiO powders was carried out up to 30 h of milling in a hardened steel vial together with 8 mm diameter hardened steel balls in the mill operated at 500 rotations per minute with a ball-to-powder weight ratio of 10:1. The optimization of milling time, milling speed and ball-to-powder weight ratio was done mainly by analyzing the variation in the structural and magnetic properties of the resulting nanocomposites in the milled powders. In order to avoid excess heating generated during dry milling, the milling process was programmed to halt for 15 min after every 15 min of operation. To understand the evolution of nanostructure in NiO–Al powders, the milled powders were collected and characterized.

The phase evolution and surface morphology of the NiO–Al powders were characterized by X-ray diffraction (XRD) obtained from high-power X-Ray diffractometer (Rigaku TTRAX III 18 kW) using Cu-K_α radiation ($\lambda = 1.54056$ Å) and field-emission scanning electron microscopy (FESEM, Zeiss Sigma) and scanning electron microscopy (SEM, Leo 1430VP.), respectively. XRD data were collected at a slow scan rate of 0.005°/s for analyzing structural parameters qualitatively. The presence of any impurity components was analyzed using energy dispersive spectrometer (EDS, Oxford) unit attached to SEM. The microstructural properties of the milled powders were analyzed using TEM (JEOL 2100) technique. Magnetic properties were characterized using vibrating sample magnetometer (VSM, LakeShore Model 7410) by performing (i) room temperature magnetic hysteresis (*M*–*H*) loops and (ii) high temperature thermomagnetization (*M*–*T*) measurements from 300 to 1200 K performed at a heating rate of 4 °C/min under an applied field of 2 kOe.

3. Results and discussion

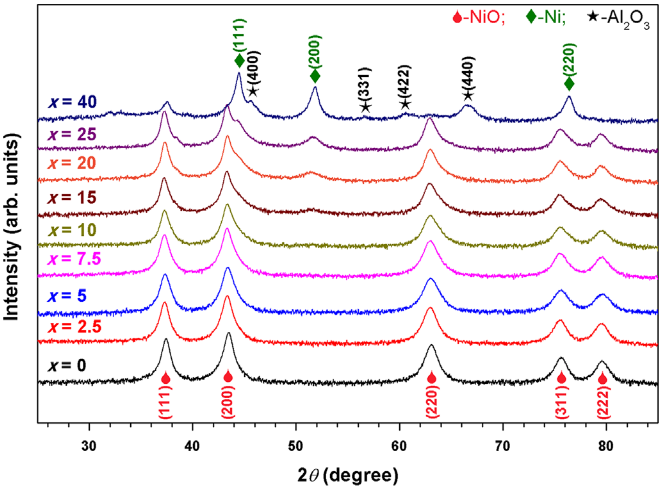

Fig. 1. Room temperature XRD patterns of 30 h milled NiO–Al (*x* wt%) powders with $x = 0$–40. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. 1 displays room temperature XRD patterns of milled NiO–Al (*x* wt%) powders with $x = 0$–40 for 30 h of milling. As-mixed NiO–Al powders (not shown here) exhibit sharp characteristic Bragg reflections corresponding to NiO (face centered cubic (*fcc*)) and Al (*fcc*). However, the Bragg reflections of Al disappear after 30 h of milling. This can be attributed to the dissolution of Al in NiO matrix. No additional Bragg peaks corresponding to any other phases or compounds were observed within the resolution of high-power XRD system. With increasing *x* up to 7.5, XRD patterns show only the peaks of NiO with large peak broadening and considerable shift in NiO(200) peak to lower angles. While the first one confirms the formation of solid solution of NiO–Al with highly-refined crystals, the later one could be attributed to the occurrence of atomic disorder due to the dissolution of Al in NiO leading to a change in the lattice parameter. On further increasing $x \geq 10$, the NiO(200) peak turns out to be asymmetric in nature and then splits into two peaks for further increase in *x* up to 25. In addition, we have observed the development of a new broad peak around $2\theta = 52°$, which grows continuously. This could be attributed to the gradual reduction of NiO by Al into Ni [15,19]. On the other hand, for the sample with $x = 40$, (i) the intensity of the Ni (111) and Ni(220) peaks increases largely along with the rapid growth of the Ni(200) peak at around $2\theta = 51.8°$, (ii) the intensity of NiO(200) peak reduces largely and submerges into Ni(111) peak, and (iii) the development of additional peaks around $2\theta = 45.6°$, 56.6°, 60.5° and 66.7° corresponding to α-Al_2O_3 phase was observed [19]. These results clearly confirm that the addition of Al in NiO forms solid solution of NiO–Al for Al up to 7.5% and then reduces NiO gradually into Ni and Al_2O_3. As a result, the color of the powder changed significantly after milling. It may be noted that the as-received pure (un-milled) NiO powder displayed pale green color, which changed into dark green after 30 h of milling. This could be attributed to the development of non-stoichiometry in NiO driven by the defects, size reduction and the oxidization of Ni^{2+} to Ni^{3+} due to breaking of Ni^{2+}–O^{2-}–Ni^{2+} symmetry [14,26–28]. With increasing *x*, the dark green color of the milled NiO powder transformed into black color due to the reduction of nanocrystalline NiO into Ni and Al_2O_3 nanocomposites. To determine the percentage of NiO reduction, we have utilized the change in the integrated intensity of NiO(200) peak [29] using $C = [(A - B)/A] \times 100$, where *A* is the integrated intensity of NiO (200) peak for the pure NiO powder, *B* is the integrated intensity of NiO(200) peak in milled NiO–Al powders and *C* is the percentage of reduction of NiO. The percentage of reduction of NiO increases gradually with increasing Al content and reaches about 50% and 91% for $x = 25$ and 40, respectively. Udhayabanu et al. [19] reported